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Metal Uptake and Bioaccumulation Potentials of *Clarias Buthupogon* and *Heterobranchus Longifilis* Collected from Asa River, Ilorin, Nigeria

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Abstract

Despite the existence of environmental legislations in Nigeria, aquatic environment has remained the sewer for wastes not minding its implications on the resident resources. Heavy metals pollution has become a worldwide concern and this may be due to their ability to bioaccumulate in aquatic organisms which is a source of livelihood for human populations. Therefore, this work aimed at assessing heavy metal accumulation in *Clarias buthupogon* and *Heterobranchus longifilis* in Asa River, Nigeria. After reconnaissance survey, fish samples were collected using hooks, traps and cast nets of various sizes twice monthly between April 2011 and March 2013 and were identified immediately. The samples were processed and heavy metal concentrations were determined in the gill, liver and muscle using atomic absorption spectrophotometer. Different metals were analysed in the gill, liver and muscle of the sampled fish species and the data obtained were subjected to statistical analysis using the T-test statistical package to determine the level of difference between means. The results in (mg kg^{-1}, dry weight) showed different levels of the analysed metals in the two fish species. The order of heavy metals accumulation in the two fish species are gills>liver>muscle and the levels of heavy metals bioaccumulation varied significantly ($p<0.05$) among season, sample locations, fish species and fish organs. All metals analysed vary significantly in the two fish species examined, seasons and across sampling sites. The results suggest that Asa River has high pollution loads of these heavy metals in fishes due to an indiscriminate of discharge of effluents in the river and could pose a health hazards to man. Consequently, close monitoring of heavy metal loads in Asa River is recommended with a view of minimizing the risks to health of the population that depend on the river for their water and fish supply.

Keywords Bioaccumulation; Heavy Metals; *Clarias buthupogon*; *Heterobranchus longifilis*; Effluent; Diversity and Species

Introduction

Bioaccumulation and biomagnifications of heavy metals in living organisms describes the processes and path-ways of pollutants from one trophic level to another. The acidic conditions of aquatic environment might cause free divalent ions of many heavy metals to be absorbed by fish gills. Health and environmental problems arising from heavy metals present in aquatic ecosystem and their bioaccumulation in fishes are very well known [1]. Heavy metals are widely distributed in water and are very essential in trace amount for normal biological and physiological activities of aquatic organisms. Heavy metals have gained much consideration among the nondegradable noxious substance owing to their poor consequences on water inhibiting fauna and flora [2]. Heavy metals are toxic substances because of their varied effects. Metals with higher concentration are known to cause harmful effects on the blood and organs of the fish. They form metals compounds when reacting with enzymes, deoxyribonucleic acid, ribonucleic acid, and cellular proteins. Chromium (Cr) in hexavalent form is comparatively active in the surrounding and is extremely toxic which may cause cancer and embryonic defects in aquatic organisms. Cr (V1) compounds are very toxic even at low concentrations but the toxicity depends on pH value of the aquatic body [3]. Limnologists are highly concerned about the increasing contaminations of water bodies due to heavy metals which are more dominant in lotic systems towards which industrial wastes are directed. Heavy metals deteriorate the ecological balance of the aquatic environment [1,4]. Because fishes are at the end of aquatic trophic level they have higher tendency to accumulate heavy metals in their body [4]. In aquatic system they diffuse radially and fish often being on the top of aquatic food chain are more susceptible to the hazardous effects as compared to terrestrial vertebrates and it is critical to investigate and monitor the bioaccumulation pattern [5]. Heavy metals bioaccumulation in fishes restricts their use as a food due to the threats they pose to health; therefore, assessment of fishes of different aquatic habitat for heavy metals accumulation is very much important.

The abnormally presence of heavy metals in organs of fish show that the aquatic environment is polluted. Heavy meals concentrations in the aquatic organism depict the past as well as the current pollution load in the environment in which the organism lives [6]. The safety of aquatic environment that makes up a major part of the environment and resources of the interested area is directly related to human health and pollution, loss of biodiversity, and habitat destruction are probably the main environmental threats for aquatic ecosystems [7].

However, fish are relatively situated at the top of the aquatic food chain; therefore, they normally can accumulate heavy metals from food, water and sediments [8]. The content of toxic heavy metals in fish can counteract their beneficial effects; several adverse effects of heavy metals to human health have been known for long time [9]. This may include serious threats like renal failure, liver damage, cardiovascular diseases and even death and therefore, many international monitoring programs have been established in order to assess the quality of fish for human consumption and to monitor the health of the aquatic ecosystem [10]. In the last few decades, the presence of heavy metals in fish have been extensively studied in different parts of the world [10] and most of these studies concentrated mainly on the heavy metals in the edible part (fish muscles), reported the distribution of metals in different organs like the liver, kidneys, heart, gonads, bone, digestive tract and brain.

Therefore, the aim of the present study is to provide comparable data on seasonality of metal abundance in the tissues of wild *Clarias buthupogon* and *Heterobranchus longifilis* collected from three sample sites covering the whole Asa River and to evaluate possible ecotoxicological and human health risks associated with fish consumption. The selected sites are considered ideal to evaluate effects of anthropogenic activities concerning metal pollution up and downstream of the river course.

Materials and Methods

Fish collection and processing

Wild males and females samples of *Clarias buthupogon* and *Heterobranchus longifilis* were collected twice monthly between April 2011 and March 2013 with the help of local fishermen from the productive portion of the sample sites, which lies between latitude 80281 and 80521N and longitude 40351 and 40451East. A total number of 516 and 501numbers of fish market sizes of *Clarias buthupogon* and *Heterobranchus longifilis* respectively were collected seasonally from the study sites. Fish were transported in an icebox (0°C-4°C) to the laboratory. The body weight (g) and total body length (cm) of each fish were measured; then fish were dissected to obtain muscle, liver, and gill samples. Tissue samples were processed for metal analysis immediately after sampling.

Metal concentrations in fish tissues

Metal concentrations (Cu, Zn, Mn, Cd, Pb, Ni, Cr and Fe) were determined in fish tissues (muscle, liver and gill) using flame atomic absorption spectrophotometer (Thermo Scientific ICE 3300, UK) provided with double beam and deuterium background corrector according to APHA [11]. All metal concentrations in fish tissues are reported in mg/kg dry weight, since dry weight rather than wet weight provides a more stable basis for comparison [12]. Tissue samples were oven dried at 105°C for 12 hours and then burned in a muffle furnace at 550°C for 16 hours. Samples were then acid digested and diluted with deionized water to known volume using the dry-ashing procedure. The QA/QC protocols included the use of analytical blanks, replicate analyses, standard solutions prepared in the same acid matrix, and standard reference material. Standards for instrument calibration were prepared on the basis of mono-element certified reference solution (Merck). Standard reference material (Lake Superior fish 1946; National Institute of Standards and Technology (NIST), USA) was used to validate analysis, and the metal average recovery percentages ranged from 93% to 107% for all measured samples. The results were expressed as mean ± SE. Data were subjected to tests for normality and homogeneity. Test for normality was positive and followed the normal distribution; also test for homogeneity showed homogenous distribution of all data within the bell shape range.

Statistical analysis

Data were statistically analysed using the statistical package for the Social Sciences (SPSS) software for IBM personal computers. The level of difference between mean values to indicate significant differences in metal levels among sites, species and season ($p<0.05$) were determined using a One-way Anova.

Results

Generally, lead (Pb), copper (Cu), zinc (Zn), cadmium (Cd), nickel (Ni), chromium (Cr) and magnesium (Mg) were analysed in the gill, liver and muscle of *C. buthupogon* and *H. longifilis* caught from the productive site of Asa River.

Heavy metal concentration in the gills

The gills of the two fish species examined from the downstream portion of the river showed that, there was a significant variation ($P<0.05$) in the amount of chromium in between the two seasons of the year while there were varied level of differences in value of each of the heavy metals in gills of *C. buthupogon* except in lead and cadmium across the two sampling sites (Table 1). In *H. longifilis*, there exist a significant seasonal deviation ($P<0.05$) in the concentrations of Cu, Cd and Ni while sample locations had significant variation on Pb, Ni, and Cr.

	Season		**Sample Location**	
Heavy Metal	**Dry**	**Rainy**	**Upstream**	**Downstream**
C. buthupogpon				
Lead (Pb)	00.07 ± 00.04	00.01 ± 00.10	00.17 ± 00.07	00.10 ± 00.08
Copper (Cu)	03.01 ± 00.36	03.82 ± 00.75	02.75 ± 00.65	03.08 ± 00.50*
Zinc (Zn)	11.19 ± 23.47	14.69 ± 31.92	12.82 ± 20.31	15.06 ± 28.09*
Cadmium (Cd)	00.68 ± 00.33	00.77 ± 00.65	00.48 ± 00.44	00.26 ± 00.59
Nickel (Ni)	00.29 ± 00.08	00.23 ± 00.16*	00.41 ± 00.07	00.32 ± 00.15*
Chromium (Cr)	00.04 ± 00.03	00.07 ± 00.06*	00.04 ± 00.04	00.01 ± 00.04*
Manesium (Mg)	00.30 ± 00.39	00.43 ± 00.28	00.46 ± 00.02	00.37 ± 00.41
H. longifilis				

Lead (Pb)	00.08 ± 00.05	00.09 ± 00.08	00.06 ± 00.06	00.10 ± 00.09*
Copper (Cu)	03.04 ± 00.46	03.74 ± 00.51*	02.79 ± 00.46	02.99 ± 00.54*
Zinc (Zn)	14.44 ± 27.21	17.12 ± 17.69	17.22 ± 17.90	14.33 ± 24.34
Cadmium (Cd)	00.11 ± 00.39	00.43 ± 00.59*	00.71 ± 00.44	00.63 ± 00.59
Nickel (Ni)	00.27 ± 00.05	00.49 ± 00.09*	0030 ± 00.07	00.25 ± 00.09*
Chromium (Cr)	00.07 ± 00.04	00.16 ± 00.05*	00.14 ± 00.03	00.08 ± 00.05*
Magnesium (Mg)	00.18 ± 00.21	00.24 ± 00.09	00.37 ± 00.30	00.30 ± 00.12
*Means significantly different at p<0.05				
Data were expressed in SEM				

Table 1: Heavy metals concentrations in the gill tissue of fish samples from Asa River.

Heavy metal concentration in the liver

The liver of fish species caught from the two sample sites along the stretch of Asa River recorded a varied level of heavy metals when statistically compared with the two seasons and sites. For *C. buthupogon*, sample location and season had significant difference (P<0.05) among all the heavy metals analysed in the liver of the fish except in Zn (Table 2) at the instance of *H. longifilis*, effects of sample locations were found to be significant (P<0.05) on each of the analysed metal in the liver except Cr: while seasonal effects were significantly different (p<0.05) in all but Ni, Cr and Mg.

	Season		Sample Location	
Heavy Metal	**Dry**	**Rainy**	**Upstream**	**Downstream**
C. buthupogpon				
Lead (Pb)	00.04 ± 00.02	00.20 ± 00.37*	00.26 ± 00.09	00.18 ± 00.37*
Copper (Cu)	04.81 ± 00.55	04.39 ± 00.89*	04.29 ± 00.67	04.10 ± 00.74*
Zinc (Zn)	61.88 ± 18.53	70.53 ± 18.27*	52.22 ± 18.92	40.19 ± 18.78*
Cadmium (Cd)	00.61 ± 00.39	00.76 ± 00.21*	00.75 ± 00.18	00.63 ± 00.24*
Nickel (Ni)	00.32 ± 00.05	00.49 ± 00.09*	00.30 ± 00.07	00.25 ± 00.09*
Chromium (Cr)	00.05 ± 00.04	00.09 ± 00.04	00.09 ± 00.07	00.06 ± 00.03*
Manesium (Mg)	00.06 ± 00.03	00.07 ± 00.07	00.14 ± 00.04	00.08 ± 00.06*
H. longifilis				
Lead (Pb)	00.04 ± 00.02	00.13 ± 00.24*	00.12 ± 00.24	00.05 ± 00.03
Copper (Cu)	02.95 ± 00.48	03.17 ± 00.75*	02.63 ± 00.78	02.59 ± 00.70
Zinc (Zn)	61.34 ± 13.89	70.91 ± 16.49*	63.10 ± 18.17	59.15 ± 13.11
Cadmium (Cd)	00.49 ± 00.19	00.66 ± 00.14*	00.45 ± 00.18	00.40 ± 00.17
Nickel (Ni)	00.28 ± 00.08	00.34 ± 00.14	00.34 ± 00.12	00.28 ± 00.11
Chromium (Cr)	00.05 ± 00.03	00.07 ± 00.15	00.04 ± 00.15	00.03 ± 00.05
Magnesium (Mg)	00.05 ± 00.04	00.07 ± 00.15	00.07 ± 00.15	00.08 ± 00.05
*Means significantly different at p<0.05				
Data were expressed in SEM				

Table 2: Heavy metals concentrations in the liver of fish samples from Asa River.

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Heavy metal concentration in the muscle

Fish muscle was also noticed to accumulate heavy metals in different trend. Different level of metal accumulation in *C. buthupogon* were observed, where sample locations had significant correlation (P<0.05) on all the heavy metals analysed in the muscle while there were also significant seasonal effects in Cu, Zn and Cd only. Meanwhile, in *H. longifilis*, there was a seasonal significant correlation (P<0.05) on Pb, Cu, Zn and Mg while the spatial effects on each of the metals analysed were significant for fish muscle except in Ni (Table 3).

	Season		Sample Location	
Heavy Metal	**Dry**	**Rainy**	**Upstream**	**Downstream**
C. buthupogpon				
Lead (Pb)	00.02 ± 00.01	00.03 ± 00.20	00.02 ± 00.01	00.06 ± 00.03*
Copper (Cu)	03.34 ± 00.66	02.98 ± 00.75*	02.77 ± 00.53	03.55 ± 00.58*
Zinc (Zn)	37.78 ± 09.32	28.94 ± 07.30*	28.51 ± 06.15	38.21 ± 09.70*
Cadmium (Cd)	00.37 ± 00.14	00.29 ± 00.23*	00.23 ± 00.10	00.44 ± 00.21*
Nickel (Ni)	00.34 ± 00.12	00.32 ± 00.11	00.27 ± 00.08	00.39 ± 00.12*
Chromium (Cr)	00.04 ± 00.03	00.05 ± 00.06	00.02 ± 00.02	00.07 ± 00.06*
Manesium (Mg)	00.08 ± 00.15	00.08 ± 00.15	00.03 ± 00.03	00.10 ± 00.14*
H. longifilis				
Lead (Pb)	00.37 ± 00.22	00.02 ± 00.12*	00.02 ± 00.01	00.04 ± 00.02*
Copper (Cu)	03.33 ± 00.34	02.58 ± 00.40*	02.82 ± 00.55	03.10 ± 00.47*
Zinc (Zn)	30.60 ± 02.14	25.06 ± 03.86*	26.59 ± 04.42	29.07 ± 03.54*
Cadmium (Cd)	00.27 ± 00.12	00.22 ± 00.15	00.22 ± 00.10	00.26 ± 00.17
Nickel (Ni)	00.25 ± 00.06	00.24 ± 00.05	00.24 ± 00.05	00.25 ± 00.06
Chromium (Cr)	00.03 ± 00.02	00.03 ± 00.02	00.02 ± 00.13	00.05 ± 00.03*
Magnesium (Mg)	00.05 ± 00.13	00.03 ± 00.03	00.03 ± 00.021	00.05 ± 00.03*
*Means significantly different at p<0.05				
Data were expressed in SEM				

Table 3: Heavy metals concentrations in the muscle of fish sample from Asa River.

Discussion

Bioaccumulations of heavy metals are used for environmental monitoring largely because aquatic organisms are in direct contact with all suspended materials in water. Tissue metal concentrations in fish are good indicators of aquatic system exposure to the metal contamination. Heavy metals accumulate in fishes via water, sediments, food such ass algae upon which both herbivorous and omnivorous fishes feed. In this present study, Pb, Cu, Zn, Cd, Ni, Cr and Mg were evaluated in the gills, liver and muscle of both *C. buthupogon* and *H. longifilis* caught from two polluted portions of Asa River. Generally, the metals in the fish organs were higher than their corresponding values in water. The metal contents also recorded large variations among the different organs and tissues of the same fish species, across the two sampling sites and across the two seasons of the year. This report corroborates the submission of [13].

High metal concentrations in the fish tissues recorded in this work could be attributed to the higher metal concentration found in the sediment of the river, which has not been investigated before now, and has been reported to be the potent site of metal accumulation in the natural environment. This could be an indication of a large quantity of metal uptake through the gills and the skin and the food chain because of the omnivorous feeding habits of these two species, as reported for the bottom feeding habits of omnivorous *Clarias gariepinus*, by APHA [14].

Present data showed that metal concentrations were highest in the gills followed by the liver and muscle. It is well known that gill is the primary site of metal contact and consequentially their absorption. However, the adsorption of metals on to the gill surface could also be an important factor in the increased levels of metals in the gill. Liver being an important organ of accumulation and detoxification of metals was second to the gills in storing heavy metals. Metal contamination of aquatic ecosystems has been recognized as a serious pollution problem. When metals are released into water surface, it tends to accumulate in the sediments through adsorption and precipitation process. It can then be reintroduced back into the water in a bio-available form with changing water quality conditions to resident fishes which eventually absorbs it from the water by means of gills or epithelial tissues and concentrates it in the body all these corroborated the findings of Fernandes et al. [15]. Metal concentrations in fishes have also been related to morphometry and pH, alkalinity, dissolved organic matter, trophic relationships of fish, as well as differences among species and fish mass within population and usually exhibit positive skewness and are frequently non-normal, this finding conformed to the data obtained in this present work. Thus, the organ level order of metal bioaccumulation in the two fish species was in the order of Gills>Liver>Muscle, which is the same as the report of Osakwe et al. [16] when *Clarias gariepinus* bio-accumulated the highest amount of metals in its gills followed by its liver, skin and muscle. The high metal concentration detected in the gills and liver in this present study, might indicate long-term (chronic) exposure of these resident fish species to these metals.

The order of lead accumulation in the different organ/parts of the two species was Gills>Liver>Muscle. The order of accumulation of Cu was given as Muscles>Gills>Liver. The order in Zn was Gills>Liver>Muscle. The order of accumulation of cadmium in the organs evaluated was Gills>Liver>Muscle. The order found in Ni was Muscle>Liver>Gill. The order found in Cr distribution was Gill>Liver>Muscle while the order of accumulation of Mg in the four organs in the two fish species was Gill>Muscle>Liver. Out of all the seven metals analysed, Zinc and Cadmium were found to be very high in the two seasons of the year and in the two sample locations. In addition, all the seven metals examined, increased in concentration in all the four tissues investigated and the source of the metals could be the discharge of effluent from various anthropogenic activities directly or indirectly into the river.

In the gills of the two fish species under investigation, the metals analysed were found in the accumulated order of Zn>Cd>Cu>Mg>Ni>Pb>Cr. Zinc was in the highest in concentration while chromium was the least. All the analysed metals increased in the gill tissue from highly polluted downstream A and decreased downstream B, and the dry season of the year also recorded high concentration of analysed metals and low concentration was obtained in the rainy season. The possible reason for the tremendous increase in the level of the individual metal level in the gill of the two species during the rainy season could be traced to run-off from agricultural activities, city sewage and other anthropogenic activities. Also increased metal concentrations in the downstream A could be linked to high pollution load recorded in this part of the river. In this present study, it was observed that gills were the primary target of the metal bioaccumulation. Fish absorbs metals from the external environment primarily through their gills [17]. Comparing metal level present in the gills with the other evaluated tissues (liver, kidney and muscle), it was observed that Lead, Nickel and chromium statistically significant in their level of accumulation in the gill of *H. longifilis* across the two sample locations and in-between the two seasons of the year, Cadmium, Copper, Nickel were found to be highly accumulated in the gill. As regards *C. buthupogon*, only chromium was found to be statistically high across the two seasons of the year and Cu, Zn, Ni, Cr and Mg were found to be highly accumulated in the gill of the same species across the two sampling points. The same trend has equally been reported by other scientists. It was also reported by Osakwe et al. [16] highest chromium, copper, nickel etc., and concentrate in the gills in comparison with other tissues like liver, muscle and skin in *C. gariepinus*. He also reported a large amount of variation amongst the different metals. The degree of these highly concentrated metals in tissue like gills, suggested that, this organs took them up more readily and rapidly.

Copper concentration in gills increased but not significant and there was a significant correlation ($p<0.05$) in the level of copper across the two seasons of the year and the two sampling points respectively. Such variation in the amount of copper was reported in the gill of rainbow-trout on exposure to sub-lethal level of copper and zinc mixtures [16]. Zinc was only found to be statistically significant across the sampling site in the case of *C. buthupogon.* Generally, zinc has a two-fold influence on the gill, namely, bio-concentration of metals and the structural cellular alterations that were noticed on the gills of *Tilapia sparmanii* [16]. Copper concentration on the other hand, fluctuated between the seasons and sample locations and this could be the result of anthropogenic activities around the river area. The gill of the fish tends to concentrate metals from the surrounding medium (water). The gills also represent the area of close proximity between the internal and external environments due to the short diffusion distance from the water to the blood, as well as the large surface area exposed to the water.

The liver of the two fish species examined in this study were found to have accumulated metals higher than the muscle with the exception of the gill tissues and higher accumulation of these metals in the liver may be attributed to the fact that the liver plays an important role in accumulation and detoxification. Exposure of fish to elevated levels of heavy metals induces the synthesis of metallothionine protein (MT), which is metal binding protein and have high affinities for heavy metals and in doing so, concentrate and regulate these metals in the liver. The high level of metal accumulation in the liver of *C. buthupogon* and *H. longifilis* may be an indication of the storage of sequestered products in it as found in *Clarias gariepinus* Since the blood passes through the liver before reacting in the systemic circulation, theoretically, the liver can remove toxicants from the blood, bio-tansform them or excrete them into the bile and thus prevent their distribution to other parts of the body. High metal concentration therefore, reflect its multi-functional role in detoxification and storage and for that reason, fish livers were analysed to prove their use as indicators of trace element pollution in the fresh water environment. In this present study, *C. buthupogon* and *H. longifilis* livers accumulated the substantial amounts of industrial and agricultural metals like lead, copper, zinc, cadmium, nickel, chromium and magnesium and the order of accumulation is zinc>copper>cadmium>Nickel>magnessium>chromium>lead. Such accumulation could be attributed to the various anthropogenic activities occurring in the river vicinity. Like the gills, all metals analysed showed a significantly increasing ($p<0.05$) trend from rainy season to dry season and this may be due to high run-offs experienced during the rainy period and it was also observed that the level of metals was significantly high in the downstream A sampling site than in downstream B, this may be linked to high pollution index recorded in the heavy metal analysis of water and sediment; all may be attributed to effluent discharges into the river [17]. The highest liver accumulated metal was zinc followed by copper, cadmium, nickel, magnesium, chromium and lead in that water, while lead was the least accumulated metal.

Least amount of chromium and lead can be correlated with the least amount of these metals recorded in the water of the fish collecting sites. Fewer amounts of these two metals in the liver of the two fish species as compared to other metals is the same as the findings of Nussey et al. [18]. This may be as results of chromium and lead forming complexes with carbonates in the water and therefore becoming less bio-availability for uptake by fish. Lead though was less in amount after chromium as compared to other analysed metals in the liver but was found to be statistically significant and this could be ascribed to the major role that the liver plays in the storage and detoxification of metals. In the same vein, high amount of other metals can be attributed to the various anthropogenic activities occurring in the vicinity of River Asa as stated earlier.

The muscle is generally suggested as the major tissue of interest under routine monitoring of environmental contamination with metals. The muscle tissues of the two fish species examined in this study also showed an increased level of all the metals analysed when compared between the two sampling sites and across the two seasons of sampling years. But in overall, the metal concentration in the muscle was found to be the least in terms of zinc compared to other investigated organs and tissues. Zinc was the highly concentrated metal, while lead, chromium, magnesium were the lowest. In numerical terms, lead concentration in muscle was noted to be second in terms of accumulation after the gills. This increase in the concentration of lead in the fish muscle could be attributed to the anthropogenic activities as earlier stated above. Moreover, the presence of detergents, pharmaceuticals and heavy transportation along the bank of Asa River and effluents of many small and large towns in the vicinity of the river could also be the possible reasons. Nickel also increased slightly in both examined samples in the muscle and the amount of nickel in the muscle of both species was the least numerically, as compared to organs and tissues like liver and gills. The concentration of chromium found in muscle in the present study was less as compared with the results from other studies [17,18]. This can be linked to the less amount of ambient chromium in the fish sampling sites of Asa River water (0.02 mg/L). The concentration of lead in the muscle was relatively low than in the liver and gills. Muscles generally showed less copper concentration as compared to liver. Fevzi [13] reported that fish muscle normally contains low concentration of copper and even at high levels of copper explosive; muscle doesn't often reflect increases in the external environment. Bio-availability of copper to the fish is influenced by a number of factors: alkalinity, hardness and pH bearing of primary importance, as well as chemical processes including absorption onto particulate matter, precipitation and complexation with inorganic and organic ligands [17].

Generally, in both dry and rainy season, the level of metals investigated was higher at the upstream location than in the downstream location. The spatial variations in the data obtained, are apparent from the fish samples collected in the dry season. The differences observed in the data suggested that metal concentrations decreased as dilution took place away from the pollution source upstream. Similar observation has been reported in Ikpoba River, Nigeria and Kabul River, Pakistan [19,20]. Seasonal variation was also observed in the data collected. Higher values were obtained in the dry season than in the rainy season, this situation is expected in view of the reduction in the pollution level in the rainy period arising from increased dilution and water flow. It was to be noted that the river is at its highest volume and flow in the rainy season.

Therefore the level of metals recorded in fishes in this work is an indication of the level of heavy metal pollution of the water and probably the sediments from which the fishes were caught. It has generally been suggested that the trace metals levels were a function of species rather than of weight, although within a given species, the trace metal level might depend upon the weight of the fish. Metal concentration in fish is the result of complex associated with uptake excretion rate and homeostasis in fish and the coefficient of variation which reflects variation among individual fish was relatively high. In summary, it is therefore suggested that a general bi-monitoring programme be established which should include hydrological and geo-morphological features, the chemical and physical water quality to further assess the quality status of Asa River. Furthermore, to avoid harmful accumulation of these metals in the human system, the gills, rivers and probably the skin of fishes should preferably be discarded while processing fish for consumption. Removal of these organs will be a judicious step as this would drastically reduce the metal intake by human.

Conclusions

It is concluded that, sampled fish species accumulated heavy metals such as lead, copper, nickel, chromium, arsenic and iron in its various organs. The gill generally has the highest metal concentration followed by muscle and the liver. The increased bio-concentration of pollutants in tissues led to more disturbed metabolism and damage to tissues and organs and to the fish inhibiting the polluted water. Despite the metals accumulative potentials of the two fish samples, fishes from Asa River are still safe for human consumption but regular monitoring of the river is necessary (especially the Asa River) which receive effluents from nearby industries and from other anthropogenic sources.

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Conflict of Interest

The authors have not declared any conflict of interest.

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